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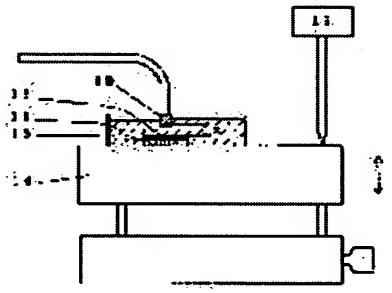
(54) METHOD FOR MEASURING CONCENTRATION DISTRIBUTION OF WATER

(57)Abstract:
PURPOSE: To measure the dielectric constant of a sample by use of a plurality of open type electrodes differed in electric length, and determined the concentration distribution of water in the depth direction of the sample from a specified formula of the obtained measured value of dielectric constant and the electric length of the electrode.
CONSTITUTION: The tip of an electrode 10 is dipped in acetone, a step pulse is used as excitation signal to measure the reflected wave by TDR method. The excitation signal and the measured reflected wave are used to calculate the dielectric spectrum while changing the value of electric length rd, and the electric length at the time the value is consistent with the known dielectric spectrum of acetone is taken as the rd of the electrode. A glass plate 11 having a fluororesin tape 12 adhered thereto is put in a water bath 13, and the electrode 10 is set in the bath so as to be opposed to the fluororesin tape 12. A Z-stage 14 is vertically moved, whereby the distance X between the electrode 10 and the tape 12 is changed, and the dielectric constant at that time is measured. The expression is established among the electric length rd of the electrode 10, the measured value εobs of dielectric constant, and the dielectric constant ε in a depth. In the expression, ε(z) represents the dielectric constant in a depth (z) from the surface.



$$\varepsilon_{obs}(\tau_d) = \frac{1}{\tau_d}\int_0^{\infty} \frac{x}{\int_0^x ds/\varepsilon(z)} \exp(-x/\tau_d)\, dx$$

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CLAIMS

[Claim(s)]
[Claim 1] The concentration distribution measuring method of the water which measures the dielectric constant of a sample using two or more open sand mold electrodes with which electric length differs, and is characterized by searching for concentration distribution of the water of the depth direction of a sample based on the relation of the measured value of a dielectric constant and the electric length of an electrode which were obtained.
[Claim 2] The measured value of a dielectric constant and the electric length of an electrode are a degree type (1).
[Equation 1]

$$\varepsilon_{obs}(\gamma d) = \frac{1}{\gamma d}\int_0^{\infty} \frac{x}{\int_0^x dz/\varepsilon(z)} \exp(-x/\gamma d)\, dx \qquad (1)$$

(-- among a formula, epsilonobs (gammad) expresses the measured value of the dielectric constant measured using the electrode of electric length gammad, and epsilon (z) expresses the dielectric constant in the depth of z from a front face.) -- concentration distribution measuring method of the water according to claim 1 which asks for relation with depth z and dielectric constant epsilon (z), and searches for concentration distribution of the water of the depth direction so that it may fill.
[Claim 3] The concentration distribution measuring method of the water according to claim 2 which searches for concentration distribution of the water of the depth direction by the inverse transformation type of a formula (1).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the concentration distribution measuring method of the water which searches for distribution of the depth direction of the concentration of the water in the sample by measuring the dielectric constant of a sample.
[0002]
[Description of the Prior Art] Generally, the property of the sample which contains water like the skin or food is greatly influenced by the moisture content. Therefore, measurement of the moisture content of these samples becomes useful [when grasping the property and condition of a sample, it is useful, and], also when evaluating the engine performance of the chemical applied to the sample, cosmetics, etc.
[0003] Then, the various water measurement approaches are proposed and used from before. For example, generally as a measuring method of the moisture of sample surfaces, such as the skin, the RF impedance method is used. However, since the RF impedance method is not observing the behavior of the water of a sample surface directly, there are many factors which affect measured value in addition to the moisture of a sample surface, and a problem is in repeatability. Moreover, the information acquired by the RF impedance method also has the problem that it is ambiguous what the depth of a thing it is, from a sample front face. Furthermore, by this approach, information about the condition of the water whether to be free water or to be bound water cannot be acquired, either.
[0004] On the other hand, as the water measurement approach of a sample surface, the dielectric constant of a sample surface is measured and the approach of measuring the dielectric relaxation of the water which exists there is proposed. As a measuring method of dielectric relaxation, although there are a frequency-domain measuring method and a time domain reflection method (it abbreviates to the TDR method (Time Domain Reflectometry method) hereafter), the latter measurement technique and research of the application are advanced positively in recent years.
[0005] This TDR method is an approach of impressing the excitation signal (for example, step pulse) of a specific wave to a sample, observing that reflected wave, asking for the complex permittivity of a sample from the phase of each frequency component of a reflected wave, and a strong change, and getting to know the physical properties of a sample based on it. For example, the example which performed a living body's water measurement by the TDR method is indicated by JP,2-110357,A (bottom right column of 17 lines of - of ten lines the 7th page of the 4th page top right column of this official report). According to this approach, since the moisture content in a sample can be measured in un-destroying and quantitatively and the information about the condition of the water whether to be free water or to be bound water can also be acquired, it is desirable.
[0006]
[Problem(s) to be Solved by the Invention] However, in the water measurement by the conventional TDR method, the average moisture content of the sample surface in a certain Mr. Fukashi cannot only pass from a sample front face to understand, and concentration distribution of the water of the depth direction of a sample cannot be known. Therefore, the problem that a chemical, cosmetics, etc. which were applied to the property of a sample, analysis of a condition, or a sample could not be evaluated was in the detail.
[0007] In addition, the tape stripping method which measures the surface of a sample as an approach of searching for concentration distribution of the depth direction of a sample while exfoliating for every predetermined depth is learned. However, such an approach has the problem that it is

accompanied by an examiner's-ed pain, when making especially the skin into a sample with destruction of a sample. Moreover, there is also a problem that concentration distribution of the depth direction cannot be searched for in sufficient precision.

[0008] When this invention tends to solve the technical problem of the above conventional techniques, a dielectric constant is measured and it performs water measurement of a sample un-destructively and quantitatively according to dielectric relaxation measurement of the TDR method etc., it aims at concentration distribution of the water of the depth direction of a sample being acquired.

[0009]

[Means for Solving the Problem] this invention person is electric merit gammad. By measuring the dielectric constant of a sample using an open sand mold electrode Depth abbreviation [from a sample front face] gammad That the average moisture content of the range can be measured Header, Furthermore, when a dielectric constant is measured using two or more open sand mold electrodes with which electric length differs to the same part of a sample, Fixed relational expression is materialized between the electric length of each electrode, and the measured value of a dielectric constant, and it came to complete a header and this invention for the ability of concentration distribution of the water of the depth direction of a sample to be searched for based on it.

[0010] That is, this invention measures the dielectric constant of a sample using two or more open sand mold electrodes with which electric merits differ, and offers the concentration distribution measuring method of the water characterized by searching for concentration distribution of the water of the depth direction of a sample based on the relation of the measured value of a dielectric constant and the electric merit of an electrode who were obtained.

[0011] Hereafter, this invention is explained to a detail based on a drawing. In addition, the same sign expresses the same or equivalent component among each drawing.

[0012] In this invention, the electrode which constitutes the field where it consists of an external electrode with which the core wire-like internal electrode was matched for the perimeter in the shape of the same axle through the insulator as the open sand mold electrode like the electrode A shown in drawing 2 or Electrode B, and the apical surface of an internal electrode and the apical surface of an external electrode touch a test portion is said.

[0013] moreover, the degree type (2) whose electric length of an electrode is the relational expression of the electromagnetic wave V (omega) and its reflected wave R (omega) concerned at the time of preparing the load of complex permittivity epsilon* (omega) in the end of the transmission line of a coaxial cable etc., and impressing the electromagnetic wave V of angular frequency omega (omega) from the other end, and complex permittivity epsilon* (omega) of a load -- setting -- parameter gammad ****** -- it is contained.

[0014]

[Equation 2]

$$\varepsilon^{*}(\omega) = \frac{c}{j\omega \cdot \gamma d} \cdot \frac{V(\omega) - R(\omega)}{V(\omega) + R(\omega)} \cdot Z \cot Z \qquad (2)$$

(式中、c＝光速度

j＝虚数単位

γd＝電気長

$Z = \omega d \sqrt{\varepsilon^{*}(\omega)} / c$

d＝伝送路の幾何学長　である。)

This electric merit gammad It can ask by measuring the reflected wave of a well-known standard sample by which complex permittivity epsilon* (omega) is known.

[0015] Moreover, electric length is the physical quantity of the electrode proper which becomes settled with the configuration and magnitude of an electrode, and is not dependent on a measuring method. Therefore, also in the measuring method of which dielectric relaxation of a frequency-domain measuring method or a time domain reflection method (the TDR method), the electric length of an electrode is fixed.

[0016] This invention is electric length gammad of such an electrode first. There is close relation to the measurement depth at the time of measuring the dielectric constant of a sample using this

electrode. Electric length gammad The measured value of the dielectric constant at the time of using an electrode is depth abbreviation [from a sample front face] gammad. It becomes the average dielectric constant of the range, therefore is electric merit gammad. It is depth abbreviation [from a sample front face] gammad by using an electrode. It is based on the knowledge that the average moisture content of the range can be measured. For example, as shown in the example 1 mentioned later, when it consists of a surface and two-layer [lower layer] and surface thickness measures dielectric relaxation about a sample equal to the electric merit of the electrode used for measurement, 63% of all the information (1-e-1) acquired with the electrode is the information from a surface.

[0017] Moreover, this invention measures a dielectric constant using two or more open sand mold electrodes with which electric length differs to the same part of a sample after being premised on the above-mentioned knowledge, and is based on the knowledge that concentration distribution of the water of the depth direction of a sample can be searched for from the relation between the electric merit obtained by that cause and the measured value of a dielectric constant. Hereafter, it explains to this ******** detail.

[0018] Electric merit gammad The value of the dielectric constant measured when an electrode is used is depth abbreviation [from a sample front face] gammad. When becoming the average value of the range If a certain relational expression can be formulized about how the dielectric constant in each depth of a sample is equalized, and actual measured value is obtained Concentration distribution of water can be calculated from the value of the electric merit at the time of measuring the dielectric constant of a sample using two or more electrodes with which electric length differs, and the measured value of a dielectric constant. Then, this formulation was tried.

[0019] In this case, first, as shown in drawing 1 (a), the common open sand mold electrode 1 which consists of external electrode 1b allotted core wire-like internal electrode 1a and internal electrode 1a, and in the shape of the same axle was made to contact Sample S, and the measurement model system in the case of measuring a dielectric constant was assumed. As shown in this drawing, by this model system, it is thought as line of electric force which comes out from the head of an electrode 1 that it exists from the thing passing through the front face of Sample S to what passes along the depths. Moreover, this model system is the capacitor c1 of the capacity [head / of an electrode 1] according to the moisture content of Sample S, c2, and c3, --, ci. It is possible that it has connected and it possible that the capacitor of a different capacity for every depth along which line of electric force passes has connected with juxtaposition in equal circuit.

[0020] Then, as Sample S is cut off by various thickness in the depth direction z and was shown in this drawing (b), each was used as the plate capacitor and this synthetic capacity was examined as an equal circuit model supposing the circuit which connected them to juxtaposition.

[0021] It sets to drawing 1 (b) and is the capacity Ci of each capacitor. c1, c2, and c3, --, ci It is equivalent to the capacity at the time of connecting a capacitor to a serial, and is [0022].

[Equation 3]

$$1/C_i = (1/c_1) + (1/c_2) + (1/c_3) + \cdots + (1/c_i)$$

It is come out and expressed. Since the capacity of a capacitor is proportional to the dielectric constant of a sample, the above-mentioned formula can be expressed also about a dielectric constant. That is, when a dielectric constant changes in the depth direction continuously, average dielectric constant epsilonav (x) to the depth x is expressed as follows.

[0023]

[Equation 4]

$$\varepsilon_{av}(x) = \frac{x}{\int_0^x dz/\varepsilon(z)}$$

When this invention person measured a dielectric constant by the various experiment systems belonging to this model system, dielectric constant epsilonav (x) found out having the weight of exp (- x/gammad) and being equalized. Then, the measured value of the dielectric constant of this model system thought that epsilonobs (gammad) was expressed with a degree type (1).

[0024]

[Equation 5]

$$\varepsilon_{obs}(\gamma d) = \frac{1}{\gamma d}\int_0^{\infty} \frac{x}{\int_0^{x} dz/\varepsilon(z)} \exp(-x/\gamma d)\, dx \qquad (1)$$

Here, epsilonobs (gammad) is electric length gammad. Expressing the measured value of the dielectric constant measured using an electrode, epsilon (z) expresses the dielectric constant in the depth of z from a front face. Moreover, the dielectric constant in this formula means the sum of dielectric constant epsiloninfinity in a field quicker enough than the relaxation time of water and relaxation on-the-strength deltaepsilon of water in dielectric constant measurement, and relaxation on-the-strength deltaepsilon of this water is proportional to the moisture content of a sample.

[0025] It is easily verifiable that this formula (1) is materialized actually about the system from which concentration distribution of water does not change in the depth direction. That is, in epsilon(x) =epsilon (regularity), it is a degree type (3) from a formula (1).

[0026]

[Equation 6]

$$\varepsilon_{obs}(\gamma d) = \varepsilon \ (\text{一定}) \qquad (3)$$

It ****** and can verify that measured-value epsilonobs in this case (gammad) is not based on the electrode to be used, but becomes fixed. Furthermore, as shown in the example later mentioned also about the two-layer system of water (surface)-Teflon (lower layer), and the two-layer system of film (upper layer)-water (surface), it was verifiable that it is actually satisfied.

[0027] therefore, concentration distribution of the depth direction of the relation of the measured value of a dielectric constant and the value of the electric merit of an electrode which measured the dielectric constant of a sample using two or more electrodes with which electric length differs in this invention, and were acquired by that cause to a sample -- asking -- facing -- dielectric constant epsilonobs (gammad) of the above-mentioned formula (1), and electric merit gammad Relational expression can be used.

[0028] During measurement of a dielectric constant, the dielectric constant of the same part of a sample is measured about the sample from which concentration distribution of water does not change with time using two or more electrodes with which electric length differs, and, more specifically, measured-value epsilonobs (gammad) of a dielectric constant is obtained for every electrode with which electric merits differ. And according to either the following approach a or the approach b, it asks for dielectric constant epsilon (x) in the depth x as concentration distribution of the water of a sample.

[0029] Approach a: A suitable function is assumed to water's concentration distribution epsilon (x), and define the parameter of the function suitably further, while changing these parameters (for example, concentration, the depth, etc. in the part by which the concentration gradient of water and the concentration of water become fixed), calculate dielectric constant epsilonobs (gammad) by the formula (1), and ask for a function and a parameter in case the calculated value and actual measured value are in agreement.

[0030] Approach b: The degree type which is an inverse transformation type of a formula (1) (4)

[0031]

[Equation 7]

$$\varepsilon(x) = \left[\frac{d}{dx}\left(\frac{x}{L^{-1}\left(\gamma d \cdot \varepsilon_{obs}(\gamma d)\right)}\right)\right]^{-1} \qquad (4)$$

(-- L-1 expresses inverse Laplace transform to s= 1/gammad among a formula.) -- it asks for water's concentration distribution epsilon (x).

[0032] In the approach of this invention, as an electrode used in order to measure a dielectric constant, it becomes an open sand mold, i.e., a core wire-like internal electrode, from the external electrode arranged on the perimeter in the shape of the same axle through the insulator, and as long as it is the electrode which constitutes the field where the apical surface of an internal electrode and the apical surface of an external electrode touch a test portion, there is especially no limit. In this case, there is especially no limit also about the apical surface configuration of an internal electrode, for example, it can consider as circular, annular, etc.

[0033] Moreover, spacing in the apical surface of an internal electrode and an external electrode may be changed suitably that what is necessary is just to change suitably the area of the electrode apical surface to which an internal electrode contacts a sample as an approach electric length obtains a mutually different electrode, for example. for example, the consistency of an impedance with the coaxial cable which will connect the electrode of 100 micrometers or less of electric merits with an electrode for the apical surface of an internal electrode at the time of measurement of a dielectric constant by [of 10 micrometers - 270 micrometers of diameters] supposing that it is circular and setting spacing of an internal electrode and an external electrode to 10 micrometers - 310 micrometers -- good -- it can obtain .

[0034] Moreover, a dielectric constant is measured using such an electrode, with either a frequency-domain measuring method or a time domain reflection method (the TDR method), the approach itself which asks for the dielectric relaxation in that case is good, and it can be based on a respectively well-known approach. For example, the measurement by the TDR method itself can be based on the well-known approach indicated by JP,2-110357,A etc.

[0035] There is especially no limit about the sample which the approach of this invention can make the measuring object. For example, that from which concentration distribution of water is changing with the depth from a sample front face can be widely made into the measuring object like the skin and food.

[0036] Moreover, there is especially no limit also about the condition of the water contained in a sample. Concentration distribution can be measured [free water] also about bound water. For example, the water shown in the example 3 mentioned later can apply the approach of this invention also to motile low water further, although the relaxation time is 10psec extent. Moreover, by the sample containing the water of two conditions, free water and bound water, concentration distribution of the depth direction of each water can be acquired by applying the approach of this invention to the dielectric constant in two frequencies.

[0037]

[Function] According to this invention, it becomes possible to search for concentration distribution of the water of the depth direction of a sample from the relation of the measured value of a dielectric constant and the electric length of an electrode which are obtained by measuring the dielectric constant of a sample using two or more electrodes with which electric length differs. Therefore, it becomes possible to evaluate in a detail the property of a sample, analysis of a condition or the chemical applied to the sample, cosmetics, etc.

[0038]

[Example] Hereafter, this invention is concretely explained based on an example.

[0039] Example 1 (i) Four electrodes E1 and E2 of A which the electrode configuration showed in this drawing as production **** of an electrode, and an electrode by a point consisting of internal electrode 1a, insulating material 1c, and external electrode 1b as shown in drawing 2 , or B, E3, and E4 It produced. Moreover, the area S1 of the radius L of the apical surface of internal electrode 1a and the apical surface of internal electrode 1a, the area S2 of the apical surface which doubled internal electrode 1a and insulating material 1c, and the bore D of the apical surface of an external electrode were made into the value shown in a table 1, respectively. Internal electrode 1a and external electrode 1b used the electrode raw material as copper, and it was filled up with Teflon between internal electrode 1a and external electrode 1b as insulating material 1c.

[0040] (ii) -- measurement of the electric length of an electrode -- the electric merit of the electrode of these was measured as follows. That is, the dielectric spectrum made the standard sample the acetone already known, dipped the head of an electrode in the acetone, and measured the reflected wave by the TDR method, using a step pulse as an excitation signal. And an excitation signal and the measured reflected wave are used and it is electric merit gammad. It considered as the parameter and the dielectric spectrum was computed from the formula (2). in this case, electric merit gammad Electric merit gammad when a dielectric spectrum is computed changing a value and the value of that computed dielectric spectrum is most in agreement with the known dielectric spectrum of an acetone Electric merit gammad of the electrode concerned ** -- it carried out. This result was shown in a table 1.

[0041]

[A table 1]

Internal electrode External electrode Internal electrode Internal electrode gammad do + Insulator electrode Configuration Radius L Bore D Area S1 Area S2 (micrometer) (micrometer) (micrometer2)

(micrometer2) (micrometer) (micrometer) E1 B 51 334 8.2x103 8.8x104 40 36E2 A 4553020 6.5x105 7.2x106290 340E3 A 255 1670 2.0x105 2.2x106 170 180E4 A 160 1050 8.0x104 8.7x105 115 130 (iii) By the related following ** of the electric merit of an electrode, and the measured value of a dielectric constant The relation between the electric merit of the electrode in the case of performing water measurement by the TDR method using these electrodes and the measurement depth of a dielectric constant is investigated, and it is electric merit gammad. The measured value of the dielectric constant at the time of using an electrode Depth abbreviation [from a sample front face] gammad In order to verify becoming the average dielectric constant of the range, various thickness of the water which is a surface was changed to the sample which consists of two-layer [of water (surface)-Teflon (lower layer)], and the dielectric constant in 100MHz was measured as follows.

[0042] That is, as shown in drawing 3 , what stuck the Teflon tape (dielectric constant 2 of Teflon) 12 on the glass plate 11 was put into the water bath (dielectric constant 78 of water) 13, and the electrode 10 was set during the bath so that the Teflon tape 12 might be countered. Moreover, this water bath 13 was laid in Z stage 14, and attached the thickness gage 15 in Z stage 14. And by making Z stage 14 go up and down, the distance x of an electrode 10 and the Teflon tape 12 was changed, and the dielectric constant at that time was measured. In this case, as a measuring method of a dielectric constant, the TDR method which makes a step pulse an excitation signal was used.

[0043] In this way, the obtained dielectric constant was shown in drawing 4 . In addition, the dielectric constant rate of change of this drawing shows the value which standardized the dielectric constant of 0 and water for the dielectric constant of Teflon with 100. Moreover, in this drawing, drawing of the lower berth is an enlarged drawing of the range of -100-400 micrometers of readings of the thickness gage of drawing of an upper case. Furthermore, the relation between -ln (1-dielectric constant rate of change) and reading of a thickness gage was shown in drawing 5 R> 5. In addition, it means moving up, while, as for the field of a value negative in reading (namely, distance x of an electrode 10 and the Teflon tape 12) of a thickness gage, the electrode 10 had contacted the Teflon tape 12 in drawing 4 and drawing 5 .

[0044] the case where the electrode 10 is in contact with the Teflon tape 12 in measurement of such a dielectric constant -- the excitation signal from an electrode 10 -- oozing out -- since it is carried out only to the Teflon tape 12, the dielectric constant observed shows constant value as shown in drawing 4 . if the electrode 10 is separated from the Teflon tape 12 and both distance x is enlarged on the other hand -- the excitation signal from an electrode 10 -- oozing out -- since the both sides of water and the Teflon tape 12 are reached, the dielectric constant observed becomes large, and if distance x is enlarged further, a dielectric constant will approach the normalization value 100 of water gradually.

[0045] The fact that the plot shows straight-line relation in a field forward in distance x in drawing 5 here shows that the dielectric constant measured is changing exponentially to distance x. That is, it is [dielectric constant / surface(water)] epsilonobs about epsilon 2 and the dielectric constant observed in the dielectric constant of epsilon 1 and a lower layer (Teflon). Dielectric constant epsilonobs which will be observed if it carries out It turns out that it is expressed with a degree type (5).

[0046]

[Equation 8]

$$\varepsilon_{obs} = \varepsilon_1 - (\varepsilon_1 - \varepsilon_2) \exp(-x/do) \qquad (5)$$

The inside of a formula, and do x is the inverse number of the slope of a line in a forward field in the plot of drawing 5 . In this way, do calculated The value was shown in a table 1. A table 1 to this do A value is above-mentioned gammad. It turns out that it is in agreement.

[0047] Then, it turns out that a formula (5) can be expressed as a degree type (6).

[0048]

[Equation 9]

$$\varepsilon_{obs} = \varepsilon_1 - (\varepsilon_1 - \varepsilon_2) \exp(-x/\gamma d) \qquad (6)$$

therefore, dielectric constant epsilonobs observed using the electrode of electric merit equal to surface(water) thickness **** -- the information on surface(water) occupies 63% of weight -- therefore -- electric merit gammad the measured value of the dielectric constant at the time of using an electrode -- depth abbreviation [from a sample front face] gammad It turns out that it becomes the average dielectric constant of the range.

[0049] (iv) -- verification of a formula (1) -- the case (refer to drawing 1) where the equal circuit of the above synthetic capacitors is considered about this system apart from this although, as for the sample which consists of two-layer [of water (surface and dielectric constant epsilon 1)-Teflon (a lower layer and dielectric constant epsilon 2)], it turned out that it is expressed like a formula (6) as mentioned above -- dielectric constant epsilon 1 of water Dielectric constant epsilon 2 of Teflon [comparing -- since it is large enough -- 0050]

[Equation 10]

$$\frac{x}{\int_0^x dz/\varepsilon(z)} = \varepsilon_1 \quad (x < x_0)$$
$$\approx \varepsilon_2 \quad (x > x_0) \qquad (7)$$

It can approximate. The inside of a formula, and x0 It is the thickness of surface water. When this formula (7) is substituted for the above-mentioned formula (1), it is a degree type (8).

[0051]

[Equation 11]

$$\varepsilon_{obs}(\gamma d) \approx \varepsilon_1 - (\varepsilon_1 - \varepsilon_2) \exp(-x_0/\gamma d) \qquad (8)$$

**********. This formula (8) is in agreement with the above-mentioned formula (6) obtained experimentally. Therefore, it sets in this system and is electric merit gammad of an electrode. Measured-value epsilonobs of a dielectric constant It was verifiable that a formula (1) is materialized between dielectric constant epsilon (z) in depth z.

[0052] Example 2 (verification of the formula (1) in the two-layer system of film (surface)-water (lower layer))

First, it is electric length gammad as an electrode. Five sorts which are 20 micrometers, 60 micrometers, 115 micrometers, 170 micrometers, and 290 micrometers were prepared.

[0053] On the other hand, as shown in drawing 6 , water (dielectric constant = 78) was filled to the upper bed of water bath 13, a flare is contacted on it, the polyvinylidene chloride film (dielectric constant = 2.4) 16 with a thickness of 10 micrometers contacted the electrode 10 on the film 16, the reflected wave was measured by the TDR method like the example 1, using a step pulse as an excitation signal, and the dielectric constant was measured. This measurement was repeated about five sorts of electrodes.

[0054] This result was plotted to drawing 7 . Moreover, it asked for the dielectric constant by performing numerical integration of a formula (1) directly. The continuous line showed this result to drawing 7 . From drawing 7 , the actual measurement of a dielectric constant and the value of the dielectric constant by the formula (1) are well in agreement. Therefore, it was verifiable that a formula (1) is materialized also in the two-layer system of this film-water.

[0055] Example 3 (analysis of concentration distribution of the water of the skin)

As an electrode, it is electric length gammad like an example 2. Five sorts which are 20 micrometers, 60 micrometers, 115 micrometers, 170 micrometers, and 290 micrometers were prepared. And the relaxation reinforcement of water was measured by the TDR method, having made the predetermined part of the healthy skin inside [forearm] people into the measuring object, and exchanging an electrode. This measurement was repeated about five sorts of electrodes.

[0056] Concentration distribution of water was searched for by two kinds of approaches, the following (a) and (b), from the obtained relaxation reinforcement.

[0057] (a) As concentration distribution of the water of the approach skin for which assumes concentration distribution of water and it asks from a formula (1), it is 0 on a front face, and it increased linearly by a certain Mr. Fukashi, and concentration assumed the model of being fixed and set to epsiloninfinity=3 in the still deeper place. And in such a model, numerical integration of a formula (1) was performed by having made into the parameter concentration of the water in the concentration gradient of the water in the range of Fukashi to whom the concentration of water becomes fixed from a front face, and the depths, it asked for the parameter by fitting, and concentration distribution of water was acquired. In this case, the sum of dielectric constant epsiloninfinity=3 by the side of a RF is set to dielectric constant epsilon (x) from the relaxation time of relaxation on-the-strength delta[of water] epsilon (x), and water. Then, it asked for the relaxation reinforcement of water by subtracting epsiloninfinity=3 from the obtained dielectric constant.

[0058] Thus, the broken line showed the acquired concentration distribution (relaxation on-the-strength deltaepsilon (x) VS. depth x of water) to drawing 8 , and the continuous line showed the

relaxation reinforcement of the water which can be found by the formula (1) in this concentration distribution to drawing 8 . Moreover, the actual measurement of the relaxation reinforcement of water was plotted to drawing 8 to electric merit. Since the actual measurement of the relaxation reinforcement of water and the relaxation reinforcement of water which can be found by the formula (1) is well in agreement from drawing 8 , it turns out that it has the concentration distribution which the skin showed to drawing 8 with the broken line.

[0059] In addition, although concentration distribution of water was expressed with the relaxation reinforcement of water to drawing 8 , the concentration of water can be obtained by dividing the relaxation reinforcement of water by 73 which is the relaxation reinforcement of 100% of water.

[0060] (b) Since it was difficult, performing inverse transformation directly from the point of measurement of the approach fraction by the inverse transformation of a formula (1) presumed the function form of epsilonobs (gammad) from measurement data, and it performed it to the function. That is, it is a degree type (9) first as a function to which fitting of the actual measurement of a dielectric constant can be carried out.

[0061]

[Equation 12]

$$\varepsilon_{obs}(\gamma d) = a_0 - \frac{a_1}{a_2 + \gamma d} + a_3 \cdot \gamma d \qquad (9)$$

(-- a0, a1, a2, and a3 assumed parameter) among the formula. Inverse Laplace transform of this formula (9) serves as a degree type (10).

[0062]

[Equation 13]

$$L^{-1}\left(\gamma d \cdot \varepsilon_{obs}(\gamma d)\right) = a_0 - \frac{a_1}{a_2} \cdot \exp\left(-\frac{x}{a_2}\right) + a_3 \cdot x \qquad (10)$$

Then, it is each parameters a0 and a1 of the above-mentioned formula (9), a2, and a3 so that the actual measurement of a dielectric constant may be suited first. It set and this asked for the formula (10). Next, this was substituted for the formula (4), the broken line showed the acquired concentration distribution to drawing 9 like the above (a) as the depth x and relation with relaxation on-the-strength delta[of water] epsilon (x), and the continuous line showed the relation of a formula (9) to drawing 9 . Moreover, the actual measurement of the relaxation reinforcement of water was plotted to drawing 9 .

[0063] By any approach of of the above (a) and (b), the front face of the skin was dried and the concentration of water increased to a depth of about 70 micrometers in monotone from the skin surface, and when deeper than it, it turned out that it is about 70 % of the weight.

[0064]

[Effect of the Invention] According to this invention, when performing water measurement of a sample un-destructively and quantitatively according to dielectric relaxation measurement of the TDR method etc., it becomes possible to acquire concentration distribution of the water of the depth direction of a sample.

[Translation done.]

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3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the explanatory view of the equal circuit of the electrode in the system of measurement of this invention.
[Drawing 2] It is the sectional view of the electrode used in the example.
[Drawing 3] It is the explanatory view of the approach of investigating the relation between the electric length of the electrode in the case of making the two-layer system of water-Teflon into a sample, and a dielectric constant.
[Drawing 4] It is related drawing of reading of a thickness gage, and dielectric constant rate of change.
[Drawing 5] It is related drawing of reading of a thickness gage, and dielectric constant rate of change.
[Drawing 6] It is the explanatory view of the approach of investigating relation with the dielectric constant measured with the electric length of the electrode in the case of making the two-layer system of film-water into a sample.
[Drawing 7] It is related drawing with the dielectric constant measured with the electric length of the electrode at the time of making the two-layer system of film-water into a sample.
[Drawing 8] It is related drawing of the depth of the sample at the time of making the skin into a sample, and relaxation reinforcement.
[Drawing 9] It is related drawing of the depth of the sample at the time of making the skin into a sample, and relaxation reinforcement.
[Description of Notations]
1 Electrode
1a Internal electrode
1b External electrode
1c Insulating material
10 Electrode
11 Glass Plate
12 Teflon Tape
13 Water Bath
14 Z Stage
15 Thickness Gage
16 Film

[Translation done.]

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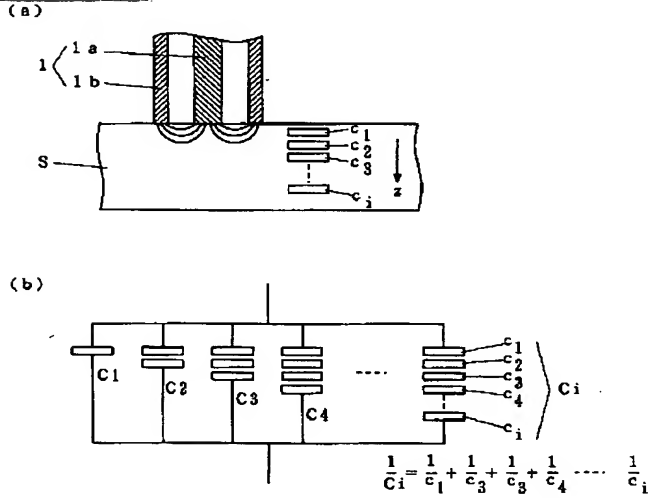
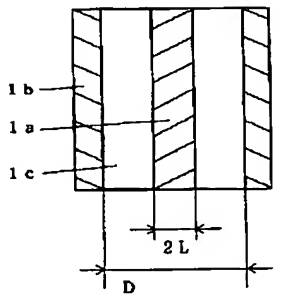
DRAWINGS

[Drawing 1]



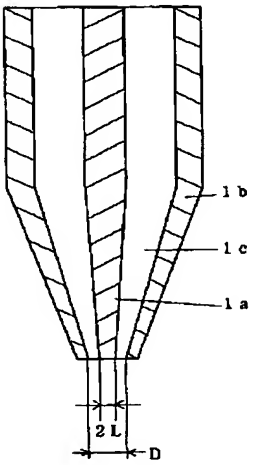
[Drawing 2]

A



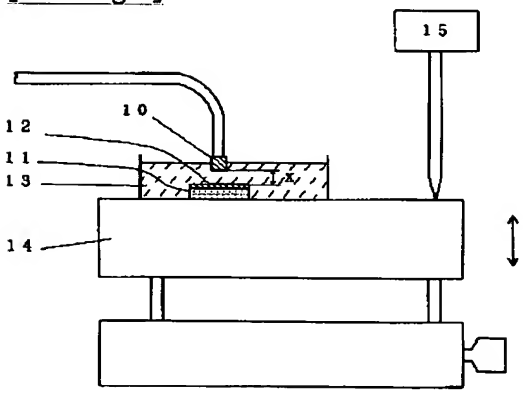
(E2, E3, E4)

B

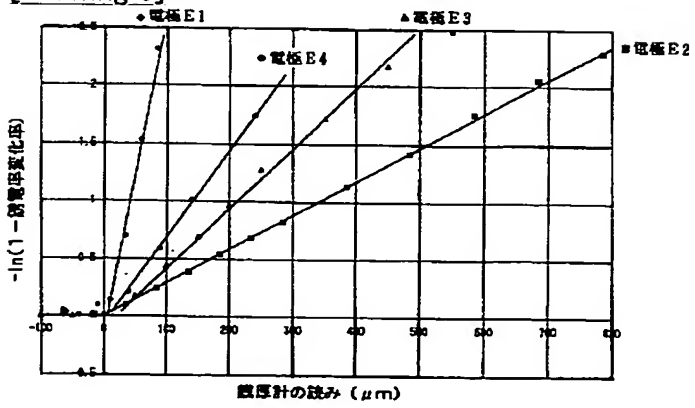


(E1)

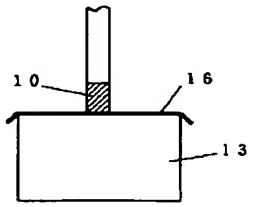
[Drawing 3]



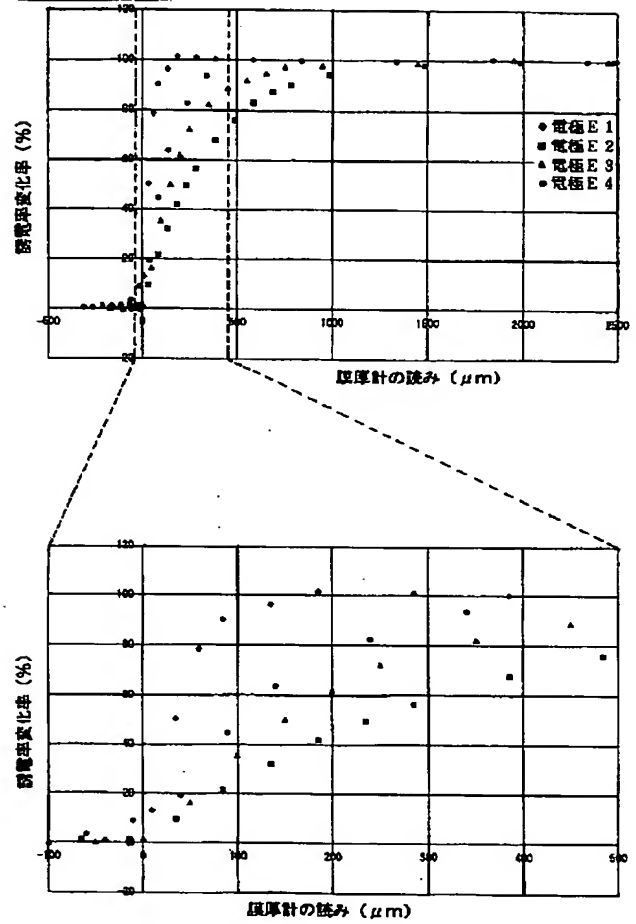
[Drawing 5]



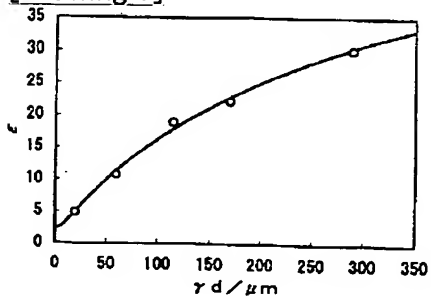
[Drawing 6]



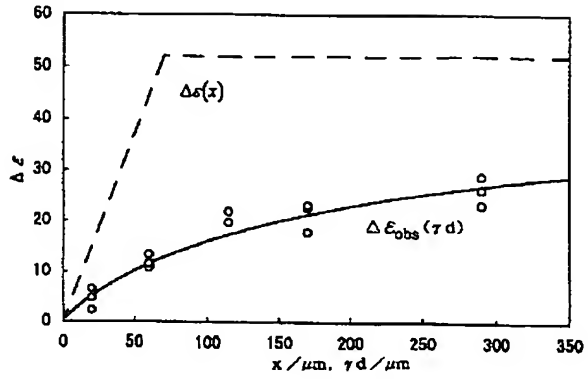
[Drawing 4]



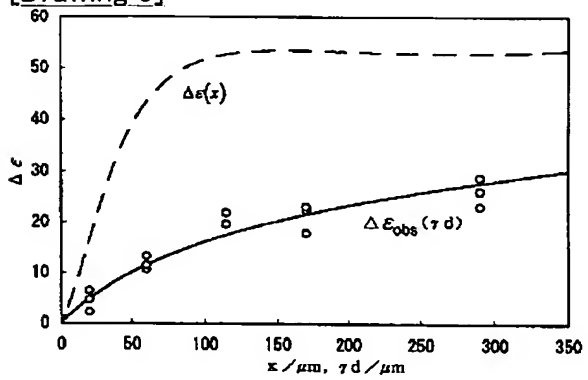
[Drawing 7]



[Drawing 8]



[Drawing 9]



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Ｇ０１Ｎ　22/00			Ｇ０１Ｎ　22/00	Ｙ	

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(54)【発明の名称】　水の濃度分布測定方法

(57)【要約】
【目的】　時間領域反射法（ＴＤＲ法）等の誘電緩和測定にしたがって試料の水分測定を非破壊的かつ定量的に行う場合に、試料の深さ方向の水の濃度分布を得られるようにする。
【構成】　電気長の異なる複数の開放型電極を用いて試料の誘電率を測定し、得られた誘電率の測定値と電極の電気長との関係に基づき、試料の深さ方向の水の濃度分布を求める。

1

【特許請求の範囲】

【請求項１】　電気長の異なる複数の開放型電極を用いて試料の誘電率を測定し、得られた誘電率の測定値と電極の電気長との関係に基づき、試料の深さ方向の水の濃度分布を求めることを特徴とする水の濃度分布測定方＊

2

＊法。

【請求項２】　誘電率の測定値と電極の電気長とが、次式（１）

【数１】

$$\varepsilon_{obs}(\gamma d)=\frac{1}{\gamma d}\int_0^{\infty}\frac{x}{\int_0^{x}dz/\varepsilon(z)}\exp(-x/\gamma d)\,dx \qquad (1)$$

（式中、ε_{obs}（γd）は電気長γdの電極を用いて測定される誘電率の測定値を表し、ε（ｚ）は表面からｚの深さにおける誘電率を表す。）を満たすように、深さｚと誘電率ε（ｚ）との関係を求め、深さ方向の水の濃度分布を求める請求項１記載の水の濃度分布測定方法。

【請求項３】　式（１）の逆変換式により深さ方向の水の濃度分布を求める請求項２記載の水の濃度分布測定方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、試料の誘電率を測定することにより、その試料中の水の濃度の深さ方向の分布を求める水の濃度分布測定方法に関する。

【０００２】

【従来の技術】一般に、皮膚や食品等のように水を含む試料の性質は、その水分含量に大きく影響される。したがって、これら試料の水分含量の測定は、試料の性質や状態を把握する上で有用であり、また、試料に適用した薬品、化粧品等の性能を評価する上でも有用となる。

【０００３】そこで、従来より種々の水分測定方法が提案され、使用されている。例えば、皮膚等の試料表層の水分の測定方法としては、一般に高周波インピーダンス法が用いられている。しかし、高周波インピーダンス法は、試料表層の水の挙動を直接的には観測していないため、試料表層の水分以外に測定値に影響を及ぼす因子が多く、再現性に問題がある。また、高周波インピーダンス法により得られる情報は、試料表面からどの程度の深さのものであるかがあいまいであるという問題もある。さらに、この方法では、自由水であるか結合水であるかという水の状態に関する情報を得ることもできない。

【０００４】これに対し、試料表層の水分測定方法としては、試料表層の誘電率を測定し、そこに存在する水の誘電緩和を測定する方法が提案されている。誘電緩和の測定方法としては、周波数領域測定法と時間領域反射法（以下、ＴＤＲ法(Time Domain Reflectometry method)と略する）とがあるが、近年、後者の測定技術及びその応用の研究が積極的に進められている。

【０００５】このＴＤＲ法は、試料に特定波形の励起信号（例えば、ステップパルス）を印加してその反射波を観測し、反射波の各周波数成分の位相と強度の変化から試料の複素誘電率を求め、それに基づいて試料の物性を知る方法である。例えば、特開平２－１１０３５７号公報には、ＴＤＲ法により生体の水分測定を行った例が記載されている（同公報第４頁上右欄１０行～第７頁下右欄１７行）。この方法によれば、試料中の水分含量を非破壊的にかつ定量的に測定することができ、また、自由水であるか結合水であるかという水の状態に関する情報も得ることができるので好ましい。

【０００６】

【発明が解決しようとする課題】しかしながら、従来のＴＤＲ法による水分測定では、単に試料表面からある深さまでの試料表層の平均的な水分含量がわかるにすぎず、試料の深さ方向の水の濃度分布を知ることはできない。そのため、試料の性質や状態の分析、あるいは試料に適用した薬品、化粧品等の評価を詳細に行うことができないという問題があった。

【０００７】なお、試料の深さ方向の濃度分布を求める方法としては、試料の表層を所定の深さごとに剥離しながら測定するテープストリッピング法が知られている。しかしながら、このような方法は試料の破壊を伴うものであり、特に皮膚を試料とする場合には、被試験者の苦痛を伴うという問題を有している。また、深さ方向の濃度分布を十分な精度で求めることができないという問題もある。

【０００８】本発明は以上のような従来技術の課題を解決しようとするものであり、誘電率を測定し、ＴＤＲ法等の誘電緩和測定にしたがって試料の水分測定を非破壊的かつ定量的に行う場合に、試料の深さ方向の水の濃度分布が得られるようにすることを目的としている。

【０００９】

【課題を解決するための手段】本発明者は、電気長γdの開放型電極を用いて試料の誘電率を測定することにより、試料表面から深さ略γd の範囲の平均的な水分含量を測定できることを見出し、さらに、試料の同一部位に対し電気長が異なる複数の開放型電極を用いて誘電率を測定した場合、各電極の電気長と誘電率の測定値との間には一定の関係式が成立し、それに基づいて試料の深さ方向の水の濃度分布を求められることを見出し、本発明を完成させるに至った。

【００１０】即ち、本発明は、電気長の異なる複数の開放型電極を用いて試料の誘電率を測定し、得られた誘電率の測定値と電極の電気長との関係に基づき、試料の深さ方向の水の濃度分布を求めることを特徴とする水の濃度分布測定方法を提供する。

3

【００１１】以下、本発明を図面に基づいて詳細に説明する。なお、各図中、同一符号は同一又は同等の構成要素を表している。

【００１２】本発明において、開放型電極とは、例えば図２に示した電極Ａ又は電極Ｂのように、芯線状の内部電極と、その周囲に絶縁体を介して同軸状に配された外部電極からなり、内部電極の先端面と外部電極の先端面とが測定試料に接する面を構成する電極をいう。

4

＊【００１３】また、電極の電気長とは、同軸ケーブル等の伝送路の一端に複素誘電率ε＊（ω）の負荷を設け、他端から角振動数ωの電磁波Ｖ（ω）を印加した場合の当該電磁波Ｖ（ω）と、その反射波Ｒ（ω）と、負荷の複素誘電率ε＊（ω）との関係式である次式（２）において、パラメータγｄとして含まれるものである。

【００１４】

【数２】

$$\varepsilon^{*}(\omega) = \frac{c}{j\omega \cdot \gamma d} \cdot \frac{V(\omega) - R(\omega)}{V(\omega) + R(\omega)} \cdot Z \cot Z \qquad (2)$$

（式中、ｃ＝光速度

ｊ＝虚数単位

γｄ＝電気長

$Z = \omega d \sqrt{\varepsilon^{*}(\omega)} / c$

ｄ＝伝送路の幾何学長　である。）

この電気長γｄは、複素誘電率ε＊（ω）が知られている公知の標準試料の反射波を測定することにより求めることができる。

【００１５】また、電気長は、電極の形状と大きさによって定まる電極固有の物理量であり、測定方法には依存しない。したがって、周波数領域測定法あるいは時間領域反射法（ＴＤＲ法）のいずれの誘電緩和の測定方法においても、電極の電気長は一定である。

【００１６】本発明は、まず、このような電極の電気長γｄと、この電極を用いて試料の誘電率を測定した場合の測定深さとには密接な関係があり、電気長γｄの電極を用いた場合の誘電率の測定値は、試料表面から深さ略γｄの範囲の平均的な誘電率となり、したがって、電気長γｄの電極を使用することにより試料表面から深さ略γｄの範囲の平均的な水分含量を測定できるという知見に基づいている。例えば、後述する実施例１に示したように、表層と下層の２層からなり、表層の厚みが、測定に使用する電極の電気長と等しい試料について誘電緩和を測定する場合、その電極で得られる全情報の６３％（$1 - e^{-1}$）が表層からの情報である。

【００１７】また、本発明は、上記の知見を前提とした上で、試料の同一部位に対し電気長が異なる複数の開放型電極を用いて誘電率を測定し、それにより得られる電気長と誘電率の測定値との関係から試料の深さ方向の水の濃度分布を求められるという知見に基づいている。以下、この点ついて詳細に説明する。

【００１８】電気長γｄの電極を用いた場合に測定される誘電率の値が試料表面から深さ略γｄの範囲の平均的※な値となる場合に、試料の各深さでの誘電率がどのように平均化されて実際の測定値が得られるかについて何等かの関係式を定式化することができれば、電気長の異なる複数の電極を用いて試料の誘電率を測定した場合の電気長の値と誘電率の測定値とから水の濃度分布を求めることができる。そこでこの定式化を試みた。

【００１９】この場合、まず、図１（ａ）に示したように、芯線状の内部電極１ａとその内部電極１ａと同軸状に配された外部電極１ｂとからなる一般的な開放型電極１を試料Ｓに当接させ、誘電率を測定する場合の測定モデル系を想定した。同図に示したように、このモデル系では、電極１の先端から出る電気力線としては、試料Ｓの表面を通るものから、深部を通るものまで存在すると考えられる。また、このモデル系は、電極１の先端に、試料Ｓの水分含量に応じた容量のコンデンサーｃ１、ｃ２、ｃ３、…、ｃｉが接続していると考えることができ、等価回路的には、電気力線の通る深さごとに異なる容量のコンデンサーが並列に接続していると考えることができる。

【００２０】そこで、試料Ｓを深さ方向ｚに種々の厚さで切り取り、同図（ｂ）に示したように、それぞれを平板コンデンサーとし、それらを並列に接続した回路を等価回路モデルとして想定し、この合成容量を検討した。

【００２１】図１（ｂ）において、各コンデンサーの容量Ｃｉは、ｃ１、ｃ２、ｃ３、…、ｃｉのコンデンサーを直列に接続した場合の容量に相当し、

【００２２】

【数３】

$$1/C_i = (1/c_1) + (1/c_2) + (1/c_3) + \cdots + (1/c_i)$$

で表される。コンデンサーの容量は、試料の誘電率に比例するため、上記の式は、誘電率についても表すことができる。即ち、誘電率が深さ方向に連続的に変化する場合、深さｘまでの平均的誘電率ε_{av}（ｘ）は次のように表される。

【００２３】

5

【数４】

$$\varepsilon_{av}(x)=\frac{x}{\int_0^x dz/\varepsilon(z)}$$

本発明者は、このモデル系に属する種々の実験系で誘電率を測定することにより、誘電率ε_{av}（ｘ）は、ｅｘｐ＊（－ｘ／ｙｄ）の重みをもって平均化されることを見出した。そこで、このモデル系の誘電率の測定値はε_{obs}（ｙｄ）は次式（１）で表されると考えた。

【００２４】

【数５】

$$\varepsilon_{obs}(\gamma d)=\frac{1}{\gamma d}\int_0^{\infty}\frac{x}{\int_0^x dz/\varepsilon(z)}\exp(-x/\gamma d)\,dx \qquad (1)$$

ここで、ε_{obs}（ｙｄ）は、電気長ｙｄの電極を用いて測定される誘電率の測定値を表し、ε（ｚ）は表面からｚの深さにおける誘電率を表す。また、この式における誘電率は、誘電率測定における水の緩和時間よりも十分に速い領域での誘電率ε_{∞}と水の緩和強度Δεとの和を意味し、この水の緩和強度Δεは、試料の含水量に比例する。

※【００２５】この式（１）が実際に成立することは、深さ方向に水の濃度分布が変化しない系については、容易に検証することができる。即ち、ε（ｘ）＝ε（一定）の場合、式（１）から次式（３）

【００２６】

【数６】

※

$$\varepsilon_{obs}(\gamma d)=\varepsilon\ (\text{一定}) \qquad (3)$$

が導出され、この場合の測定値ε_{obs}（ｙｄ）は、使用する電極によらず一定となることが検証できる。さらに、水（表層）－テフロン（下層）の２層系や、フィルム（上層）－水（表層）の２層系についても後述する実施例に示したように、実際に満足されることが検証できた。

【００２７】したがって、本発明において電気長の異なる複数の電極を用いて試料の誘電率を測定し、それにより得られた誘電率の測定値と電極の電気長の値との関係から試料の深さ方向の濃度分布を求めるに際しては、上記式（１）の誘電率ε_{obs}（ｙｄ）と電気長ｙｄとの関係式を使用することができる。

【００２８】より具体的には、誘電率の測定中、水の濃度分布が経時的に変化しない試料について、電気長の異なる複数の電極を用いて試料の同一部位の誘電率を測定★し、電気長の異なる電極ごとに誘電率の測定値ε_{obs}（ｙｄ）を得る。そして次の方法ａ又は方法ｂのいずれかにしたがい、試料の水の濃度分布として、深さｘにおける誘電率ε（ｘ）を求める。

【００２９】方法ａ：水の濃度分布ε（ｘ）に対して適当な関数を仮定し、さらにその関数のパラメータを適宜定め（例えば、水の濃度勾配、水の濃度が一定になる部位での濃度や深さ等）、これらパラメータを変化させながら式（１）により誘電率ε_{obs}（ｙｄ）を計算し、その計算値と実際の測定値とが一致する場合の関数とパラメータを求める。

【００３０】方法ｂ：式（１）の逆変換式である次式（４）

【００３１】

【数７】

$$\varepsilon(x)=\left[\frac{d}{dx}\left(\frac{x}{L^{-1}\left(\gamma d\cdot\varepsilon_{obs}(\gamma d)\right)}\right)\right]^{-1} \qquad (4)$$

（式中、L^{-1}は、ｓ＝１／ｙｄに対しての逆ラプラス変換を表す。）により水の濃度分布ε（ｘ）を求める。

【００３２】本発明の方法において、誘電率を測定するために使用する電極としては、開放型、即ち、芯線状の内部電極と、その周囲に絶縁体を介して同軸状に配された外部電極からなり、内部電極の先端面と外部電極の先端面とが測定試料に接する面を構成する電極である限り特に制限はない。この場合、内部電極の先端面形状についても特に制限はなく、例えば、円形、環状等とすることができる。

【００３３】また、電気長が互いに異なる電極を得る方法としては、例えば、内部電極が試料に接触する電極先端面の面積を適宜変えればよく、また、内部電極と外部電極との先端面における間隔を適宜変えてもよい。例えば、内部電極の先端面を径１０μｍ～２７０μｍの円形とし、内部電極と外部電極との間隔を１０μｍ～３１０μｍとすることにより、電気長１００μｍ以下の電極を、誘電率の測定時に電極と接続することとなる同軸ケーブルとのインピーダンスの整合性よく得ることができる。

【００３４】また、このような電極を用いて誘電率を測定し、その際の誘電緩和を求める方法自体は、周波数領域測定法あるいは時間領域反射法（ＴＤＲ法）のいずれによってもよく、それぞれ公知の方法によることができる。例えば、ＴＤＲ法による測定自体は、特開平２－１１０３５７号公報等に記載されている公知の方法による

7

ことができる。

【００３５】本発明の方法が測定対象とすることができる試料については特に制限はない。例えば、皮膚、食品等のように、試料表面からの深さにより水の濃度分布が変化しているものを広く測定対象とすることができる。

【００３６】また、試料中に含有される水の状態についても特に制限はない。自由水についても結合水についても濃度分布を測定することができる。例えば、後述する実施例３に示した水は、緩和時間が１０ｐｓｅｃ程度であるが、さらに運動性の低い水に対しても本発明の方法を適用することができる。また、自由水と結合水の２つの状態の水を含有する試料では、２つの周波数における誘電率に対して本発明の方法を適用することにより、それぞれの水の深さ方向の濃度分布を得ることができる。

【００３７】

【作用】本発明によれば、電気長の異なる複数の電極を用いて試料の誘電率を測定することにより得られる誘電率の測定値と電極の電気長との関係から、試料の深さ方向の水の濃度分布を求めることが可能となる。したがって、試料の性質や状態の分析、あるいは試料に適用した薬品、化粧品等の評価を詳細に行うことが可能となる。

【００３８】

【実施例】以下、本発明を実施例に基づいて具体的に説明する。

【００３９】実施例１

8

＊(i) 電極の作製

まず、電極として、図２に示したように、先端部が内部電極１ａ、絶縁材１ｃ及び外部電極１ｂからなり、電極形状が同図に示したＡ又はＢの４つの電極Ｅ1、Ｅ2、Ｅ3、Ｅ4を作製した。また、内部電極１ａの先端面の半径Ｌ、内部電極１ａの先端面の面積Ｓ1、内部電極１ａと絶縁材１ｃとを合わせた先端面の面積Ｓ2、及び外部電極の先端面の内径Ｄは、それぞれ表１に示した値とした。電極素材は、内部電極１ａ、外部電極１ｂ共に銅とし、絶縁材１ｃとしては内部電極１ａと外部電極１ｂとの間にテフロンを充填した。

【００４０】(ii)電極の電気長の測定

これらの電極の電気長を次のようにして測定した。即ち、誘電スペクトルが既に知られているアセトンを標準試料とし、電極の先端をアセトンに浸し、励起信号としてステップパルスを用いてＴＤＲ法で反射波を測定した。そして、励起信号と測定された反射波とを用い、電気長γｄをパラメータとして、式（２）から誘電スペクトルを算出した。この場合、電気長γｄの値を変えながら誘電スペクトルを算出し、その算出した誘電スペクトルの値がアセトンの既知の誘電スペクトルと最も一致した場合の電気長γｄを当該電極の電気長γｄとした。この結果を表１に示した。

【００４１】

＊【表１】

電極	形状	内部電極 半径Ｌ（μｍ）	外部電極 内径Ｄ（μｍ）	内部電極 面積Ｓ1（μｍ²）	内部電極＋絶縁体 面積Ｓ2（μｍ²）	γｄ（μｍ）	ｄｏ（μｍ）
Ｅ1	Ｂ	51	334	8.2×10^{3}	8.8×10^{4}	40	36
Ｅ2	Ａ	455	3020	6.5×10^{5}	7.2×10^{6}	290	340
Ｅ3	Ａ	255	1670	2.0×10^{5}	2.2×10^{6}	170	180
Ｅ4	Ａ	160	1050	8.0×10^{4}	8.7×10^{5}	115	130

(iii) 電極の電気長と誘電率の測定値との関係

次いで、これら電極を用いてＴＤＲ法により水分測定を行う場合の電極の電気長と誘電率の測定深さとの関係を調べ、電気長γｄの電極を用いた場合の誘電率の測定値は、試料表面から深さ略γｄの範囲の平均的な誘電率となることを検証するために、水（表層）－テフロン（下層）の２層からなる試料に対して表層である水の厚みを種々変えて１００ＭＨｚにおける誘電率を次のように測定した。

【００４２】即ち、図３に示したように、ガラス板１１にテフロンテープ（テフロンの誘電率２）１２を貼ったものを、水浴（水の誘電率７８）１３に入れ、そのテフロンテープ１２に対向するように浴中に電極１０をセットした。また、この水浴１３はＺステージ１４に載置し、Ｚステージ１４には膜厚計１５を取り付けた。そして、Ｚステージ１４を上下させることにより、電極１０とテフロンテープ１２との距離ｘを変化させ、そのときの誘電率を測定した。この場合、誘電率の測定方法としては、ステップパルスを励起信号とするＴＤＲ法を用いた。

【００４３】こうして得られた誘電率を図４に示した。なお、同図の誘電率変化率は、テフロンの誘電率を０、水の誘電率を１００と規格化した値を示している。また、同図において下段の図は上段の図の膜厚計の読み－１００～４００μｍの範囲の拡大図である。さらに、図５に、－ｌｎ（１－誘電率変化率）と膜厚計の読みとの関係を示した。なお、図４、図５において膜厚計の読み（即ち、電極１０とテフロンテープ１２との距離ｘ）が

9

負の値の領域は、電極１０がテフロンテープ１２に接触したまま上方に移動していることを表している。

【００４４】このような誘電率の測定においては、電極１０がテフロンテープ１２に接している場合には、電極１０からの励起信号の滲み出しはテフロンテープ１２のみに行われるので、図４に示されているように、観測される誘電率は一定値を示す。一方、電極１０をテフロンテープ１２から離していき、両者の距離ｘを大きくしていくと、電極１０からの励起信号の滲み出しは水とテフロンテープ１２の双方に及ぶので、観測される誘電率は大きくなり、さらに距離ｘを大きくしていくと次第に誘＊

式中、ｄｏは、図５のプロットでｘが正の領域における直線の傾きの逆数である。こうして求められるｄｏの値を表１に示した。表１から、このｄｏの値は、上述のγｄと一致することがわかる。※

したがって、表層（水）の厚さに等しい電気長の電極を用いて観察される誘電率ε_{obs}には、表層（水）の情報が６３％の重みを占めること、よって、電気長γｄの電極を用いた場合の誘電率の測定値は、試料表面から深さ略γｄの範囲の平均的な誘電率となることがわかる。

【００４９】(iv)式（１）の検証

上記のように、水（表層、誘電率ε_1）ーテフロン（下★

$$\frac{x}{\int_0^x dz/\varepsilon(z)} = \varepsilon_1 \quad (x < x_0)$$
$$\approx \varepsilon_2 \quad (x > x_0)$$

と近似することができる。式中、x_0は表層の水の厚みである。この式（７）を前述の式（１）に代入すると次式（８）☆

$$\varepsilon_{obs}(\gamma d) \approx \varepsilon_1 - (\varepsilon_1 - \varepsilon_2)\exp(-x_0/\gamma d) \qquad (8)$$

が得られる。この式（８）は実験的に得られた前述の式（６）と一致する。したがって、この系において、電極の電気長γｄと誘電率の測定値ε_{obs}と深さｚにおける誘電率ε（ｚ）との間に式（１）が成立することが検証できた。

【００５２】実施例２（フィルム（表層）ー水（下層）の２層系における式（１）の検証）

まず、電極として、電気長γｄが２０μｍ、６０μｍ、１１５μｍ、１７０μｍ、２９０μｍの５種を用意した。

【００５３】一方、図６に示すように、水浴１３の上端まで水（誘電率＝７８）を満たし、その上に厚さ１０μｍのポリ塩化ビニリデンフィルム（誘電率＝２．４）１６を張り、そのフィルム１６に電極１０を接触させ、実施例１と同様に励起信号としてステップパルスを用いてＴＤＲ法により反射波を測定し、誘電率を測定した。この測定を５種の電極について繰り返した。

10

＊電率は水の規格化値１００に近付く。

【００４５】ここで、図５において、距離ｘが正の領域において、プロットが直線関係を示していることから、測定される誘電率は距離ｘに対して指数関数的に変化していることがわかる。即ち、表層（水）の誘電率をε_1、下層（テフロン）の誘電率をε_2、観測される誘電率をε_{obs}とすると、観測される誘電率ε_{obs}は、次式（５）で表されることがわかる。

【００４６】

【数８】

$$\varepsilon_{obs} = \varepsilon_1 - (\varepsilon_1 - \varepsilon_2)\exp(-x/do) \qquad (5)$$

※【００４７】そこで、式（５）は次式（６）と表せることがわかる。

【００４８】

【数９】

$$\varepsilon_{obs} = \varepsilon_1 - (\varepsilon_1 - \varepsilon_2)\exp(-x/\gamma d) \qquad (6)$$

★層、誘電率ε_2）の２層からなる試料は、式（６）のように表されることがわかったが、これとは別に、この系について前述のような合成コンデンサーの等価回路を考えた場合（図１参照）、水の誘電率ε_1はテフロンの誘電率ε_2に比して十分に大きいため、

【００５０】

【数１０】

$$\frac{x}{\int_0^x dz/\varepsilon(z)} = \varepsilon_1 \quad (x < x_0)$$
$$\approx \varepsilon_2 \quad (x > x_0)$$

（７）

☆【００５１】

【数１１】

$$\varepsilon_{obs}(\gamma d) \approx \varepsilon_1 - (\varepsilon_1 - \varepsilon_2)\exp(-x_0/\gamma d) \qquad (8)$$

【００５４】この結果を図７にプロットした。また、式（１）の数値積分を直接行うことにより誘電率を求めた。この結果を図７に実線で示した。図７から、誘電率の実測値と式（１）による誘電率の値とはよく一致している。したがって、このフィルムー水の２層系においても式（１）が成立することが検証できた。

【００５５】実施例３（皮膚の水の濃度分布の解析）

電極として、実施例２と同様に、電気長γｄが２０μｍ、６０μｍ、１１５μｍ、１７０μｍ、２９０μｍの５種を用意した。そして、人の前腕内側の健常な皮膚の所定箇所を測定対象とし、電極を取り替えながら、ＴＤＲ法により水の緩和強度を測定した。この測定を５種の電極について繰り返した。

【００５６】得られた緩和強度から次の（ａ）、（ｂ）の２通りの方法により水の濃度分布を求めた。

【００５７】（ａ）水の濃度分布を仮定して式（１）から求める方法

11

皮膚の水の濃度分布として、濃度が表面で０であり、ある深さまで直線的に増加し、さらに深いところでは一定であるというモデルを仮定し、$\varepsilon\infty=3$とした。そして、このようなモデルにおいて、表面から水の濃度が一定となる深さまでの範囲における水の濃度勾配、深部における水の濃度をパラメータとして、式（１）の数値積分を行い、フィッティングによりパラメータを求め、水の濃度分布を得た。この場合、水の緩和強度$\Delta\varepsilon$（ｘ）と水の緩和時間よりも高周波側の誘電率$\varepsilon\infty=3$との和が誘電率ε（ｘ）となる。そこで、得られた誘電率から$\varepsilon\infty=3$を引くことにより、水の緩和強度を求めた。

【００５８】このようにして得られた濃度分布（水の緩和強度$\Delta\varepsilon$（ｘ） VS. 深さｘ）を、図８に破線で示し、この濃度分布の場合に式（１）により求まる水の緩和強度を図８に実線で示した。また、水の緩和強度の実測値＊

12

＊を電気長に対して図８にプロットした。図８から、式（１）により求まる水の緩和強度と水の緩和強度の実測値とがよく一致していることから、皮膚が図８に破線で示した濃度分布を有していることがわかる。

【００５９】なお、図８には水の濃度分布を水の緩和強度で表したが、水の緩和強度を水１００％の緩和強度である７３で割ることにより水の濃度を得ることができる。

【００６０】（ｂ）式（１）の逆変換による方法

少数の測定点から直接逆変換を行うことは難しいため、ε_{obs}（γd）の関数形を測定データから推定し、その関数に対して行った。即ち、まず、誘電率の実測値をフィッティングさせることができる関数として、次式（９）

【００６１】

【数１２】

$$\varepsilon_{obs}(\gamma d)=a_0-\frac{a_1}{a_2+\gamma d}+a_3\cdot\gamma d \qquad (9)$$

（式中、a_0、a_1、a_2、a_3はパラメータ）を想定した。この式（９）の逆ラプラス変換は次式（１０）となる。

※【００６２】

【数１３】

※

$$L^{-1}\left(\gamma d\cdot\varepsilon_{obs}(\gamma d)\right)=a_0-\frac{a_1}{a_2}\cdot\exp\left(-\frac{x}{a_2}\right)+a_3\cdot x \qquad (10)$$

そこで、まず誘電率の実測値と合うように、上記式（９）の各パラメータa_0、a_1、a_2、a_3を定め、これにより式（１０）を求めた。次に、これを式（４）に代入し、得られた濃度分布を、上記（ａ）と同様に、深さｘと水の緩和強度$\Delta\varepsilon$（ｘ）との関係として図９に破線で示し、式（９）の関係を図９に実線で示した。また、水の緩和強度の実測値を図９にプロットした。

【００６３】以上の（ａ）、（ｂ）のいずれの方法によっても、皮膚の表面は乾燥しており、皮膚表層から深さ７０μｍ程度までは水の濃度は単調に増加し、それよりも深いところでは、約７０重量％であることがわかった。

【００６４】

【発明の効果】本発明によれば、ＴＤＲ法等の誘電緩和測定にしたがって試料の水分測定を非破壊的かつ定量的に行う場合に、試料の深さ方向の水の濃度分布を得ることが可能となる。

【図面の簡単な説明】

【図１】本発明の測定系での電極の等価回路の説明図である。

【図２】実施例で用いた電極の断面図である。

【図３】水ーテフロンの２層系を試料とする場合の電極の電気長と誘電率との関係を調べる方法の説明図である。

【図４】膜厚計の読みと誘電率変化率との関係図である。

【図５】膜厚計の読みと誘電率変化率との関係図である。

【図６】フィルムー水の２層系を試料とする場合の電極の電気長と測定される誘電率との関係を調べる方法の説明図である。

【図７】フィルムー水の２層系を試料とした場合の電極の電気長と測定される誘電率との関係図である。

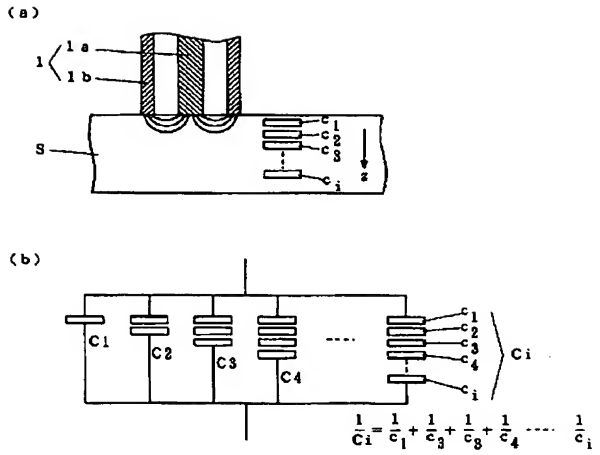
【図８】皮膚を試料とした場合の試料の深さと緩和強度との関係図である。

【図９】皮膚を試料とした場合の試料の深さと緩和強度との関係図である。

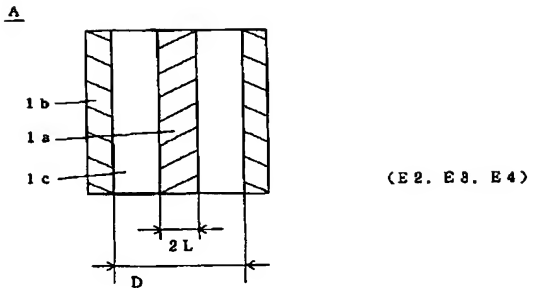
【符号の説明】

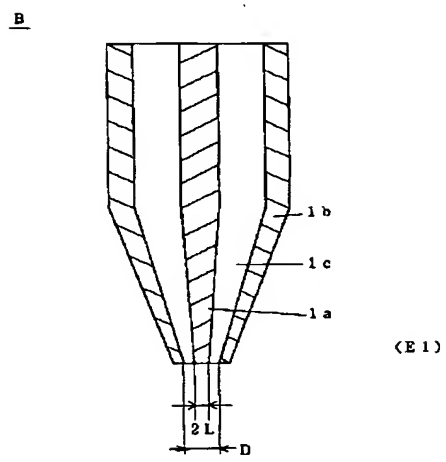
１	電極
１ａ	内部電極
１ｂ	外部電極
１ｃ	絶縁材
１０	電極
１１	ガラス板
１２	テフロンテープ
１３	水浴
１４	Ｚステージ
１５	膜厚計
１６	フィルム

【図１】

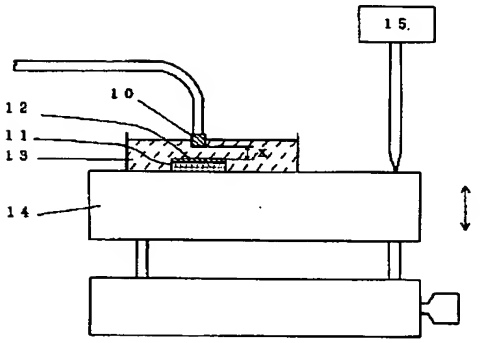

(a)
1
1a
1b
S
c1
c2
c3
ci
z
(b)
C1
C2
C3
C4
Ci
$\frac{1}{Ci}=\frac{1}{c_1}+\frac{1}{c_2}+\frac{1}{c_3}+\frac{1}{c_4}\cdots\cdots\frac{1}{c_i}$

【図２】

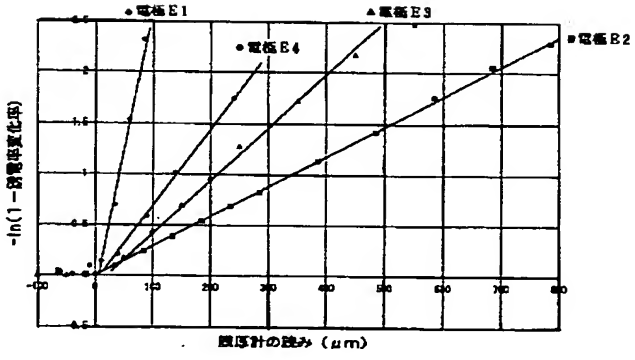

A
1b
1a
1c
2L
D
(E2, E3, E4)


B
1b
1c
1a
2L
D
(E1)

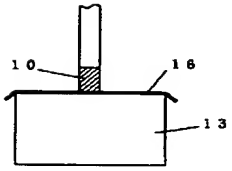
【図３】


15
10
12
11
13
14

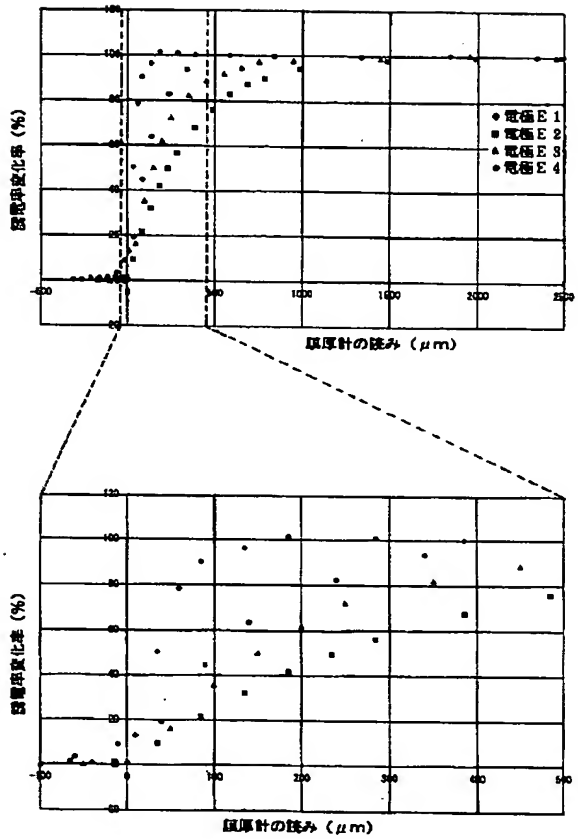
【図５】


●電極E1
▲電極E3
●電極E4
●電極E2
-ln(1-膜厚変化率)
膜厚計の読み（μm）

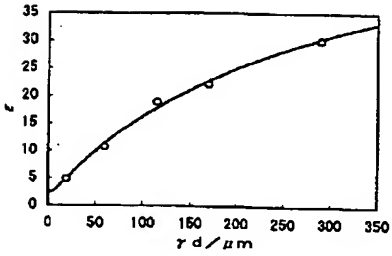
【図６】


10
16
13

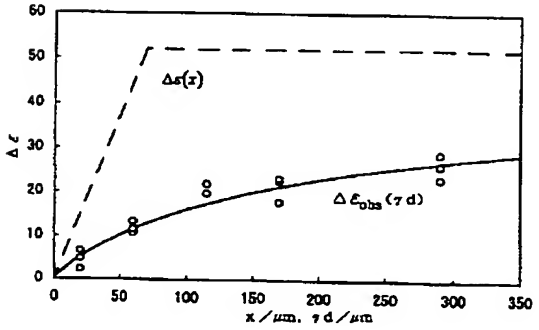
【図４】


膜厚計の読み（μm）
膜厚相対変化率（%）
電極Ｅ１
電極Ｅ２
電極Ｅ３
電極Ｅ４

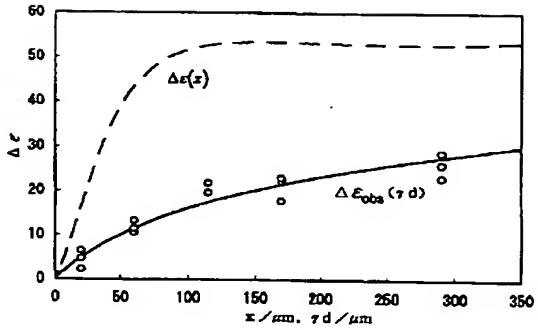
【図７】


ε
γｄ／μｍ

【図８】


Δε
Δε(x)
Δε_obs(γd)
x／μm，γd／μm

【図９】


Δε
Δε(x)
Δε_obs(γd)
x／μm，γd／μm